

# PATENT ABSTRACTS OF JAPAN

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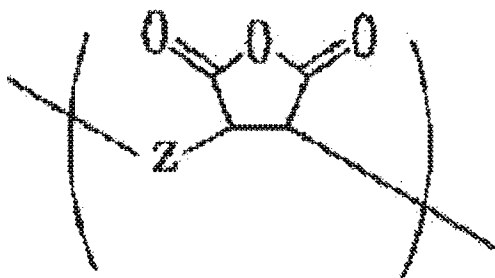
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(54) RESIN FOR RESIST, AND CHEMICAL AMPLIFICATION-TYPE RESIST,  
AND PATTERN FORMATION METHOD USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a resin for a resist which is highly transparent to far ultraviolet rays having wavelengths of about 220 nm or lower and high etching resistance and is excellent in adhesion to a substrate; and a chemical amplification-type resist and to provide a pattern formation method using the resist.

SOLUTION: This resin for a resist has an alicyclic lactone structure of formula (1) (wherein Z is an alicyclic hydrocarbon group having a lactone structure) in the main chain and has acid-decomposable groups which are decomposed by the action of an acid, increasing the solubility in an aqueous alkali solution.



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CLAIMS

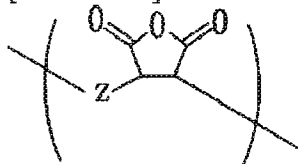
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[Claim(s)]

[Claim 1] Resin for resist which is resin for resist in which an acidolysis nature group decomposes by operation of acid, and solubility to an alkaline aqueous solution increases, and is characterized by having alicyclic lactone structure in a main chain.

[Claim 2] The resin for resist according to claim 1, wherein said alicyclic lactone structure is expressed with a general formula (1).

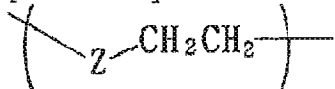
[Formula 1]



(1) (in an upper type, Z is an alicyclic hydrocarbon group which has lactone structure.)

[Claim 3] The resin for resist according to claim 1, wherein said alicyclic lactone structure is expressed with a general formula (2).

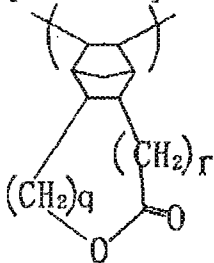
[Formula 2]



(2) (in an upper type, Z is an alicyclic hydrocarbon group which has lactone structure.)

[Claim 4] The resin for resist according to claim 1, wherein said alicyclic lactone structure is expressed with a general formula (3).

[Formula 3]

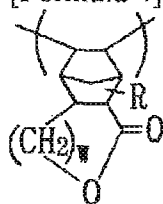


(3) (in an upper type, q is a positive integer of 0, or 1-3, and r is 1 or 2.)

[Claim 5] The resin for resist according to claim 1, wherein said alicyclic lactone structure

is expressed with a general formula (4).

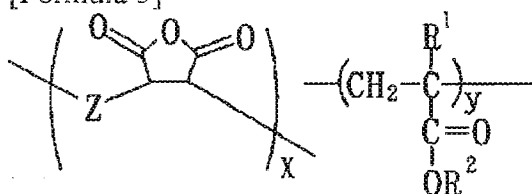
[Formula 4]



(4) (in an upper type, R is an alkyl group of the carbon numbers 1-4, and w is a positive integer of 1-3.)

[Claim 6]The resin for resist according to claim 1, wherein resin which has alicyclic lactone structure is expressed with said main chain by a general formula (5).

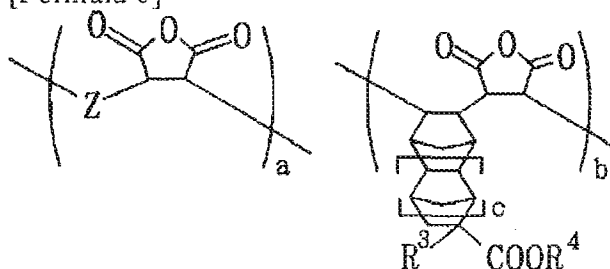
[Formula 5]



(5) (in an upper type, the alicyclic hydrocarbon group with which Z has lactone structure, and  $R^1$  express the bridged cyclic hydrocarbon group of the carbon numbers 7-13 which have a hydrogen atom or a methyl group, a basis that decomposes  $R^2$  with acid, or a basis decomposed with acid.) x and y are arbitrary numbers which fill  $x+y=1$ ,  $0 < x < 1$ , and  $0 < y < 1$ , respectively.

[Claim 7]The resin for resist according to claim 1, wherein resin which has alicyclic lactone structure is expressed with said main chain by a general formula (6).

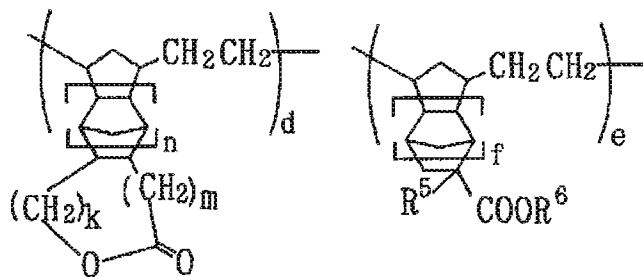
[Formula 6]



(6) (in an upper type, the alicyclic hydrocarbon group with which Z has lactone structure, and  $R^3$  express a hydrogen atom or a methyl group, and the basis that decomposes  $R^4$  with acid.) a and b are arbitrary numbers which fill  $a+b=1$ ,  $0 < a < 1$ , and  $0 < b < 1$ , respectively. c is 0 or 1.

[Claim 8]The resin for resist according to claim 1, wherein resin which has alicyclic lactone structure is expressed with said main chain by a general formula (7).

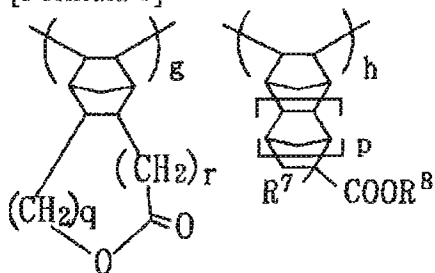
[Formula 7]



(7) (in an upper type, 0 or 1, and  $R^5$  express the basis into which the positive integer of 0, or 1-3 decomposes  $k$  into, and, as for  $m$ , 0 or 1 or  $2n$ , and  $f$  decompose a hydrogen atom or a methyl group, and  $R^6$  with acid, respectively.)  $d$  and  $e$  are arbitrary numbers which fill  $d+e=1$ ,  $0 < d < 1$ , and  $0 < e < 1$ , respectively.

[Claim 9]Resin for resist of claim 1 \*\*, wherein resin which has alicyclic lactone structure is expressed with said main chain by a general formula (8).

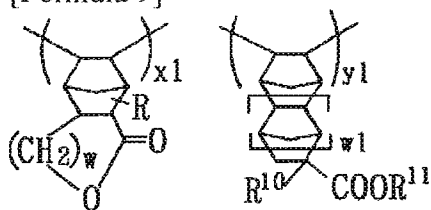
[Formula 8]



(8) In [top type, 0 or 1 (however,  $p$  is 1 when  $r$  is 0.), and  $R^7$  express the basis into which the positive integer of 0, or 1-3 decomposes  $q$  into, and, as for  $r$ , 0, or 1 or  $2p$  decomposes a hydrogen atom or a methyl group, and  $R^8$  with acid.  $g$  and  $h$  are arbitrary numbers which fill  $g+h=1$ ,  $0 < g < 1$ , and  $0 < h < 1$ , respectively. ]

[Claim 10]The resin for resist according to claim 1, wherein resin which has alicyclic lactone structure is expressed with said main chain by a general formula (9).

[Formula 9]



(9) (in an upper type, the basis into which  $w$  decomposes  $R$  into by the alkyl group of the carbon numbers 1-4, the positive integer of 1-3 decomposes it into, and, as for  $w1$ , 0 or 1, and  $R^{10}$  decompose a hydrogen atom or a methyl group, and  $R^{11}$  with acid is expressed.)  $x1$  and  $y1$  -- respectively --  $x1+y1=1$  and  $0 < x1 < 1$  -- they are the arbitrary numbers which fill 1 and  $0 < y1 < 1$ .

[Claim 11]A positive type chemical amplification type resist which contains at least resin for resist given in 1, and a photo-oxide generating agent which generates acid by exposure in either of claims 1 thru/or 10.

[Claim 12]A pattern formation method including a process of applying the chemical

amplification type resist according to claim 11 on a processing substrate, a process of exposing said processing substrate with light with a wavelength of 180-220 nm, a process of carrying out bake of said processing substrate, and a process of developing said processing substrate.

[Claim 13]The pattern formation method according to claim 12, wherein said exposing light is ArF excimer laser light.

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#### **DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the pattern formation method which used resin for resist, chemical amplification type resist, and it, and relates to the resin for resist which makes exposing light the far ultraviolet ray of the wavelength not more than abbreviated 220nm, chemical amplification type resist, and the pattern formation method using it in detail.

[0002]

[Description of the Prior Art]In manufacture of the semiconductor device represented with LSI (large scale integration circuit). Photolithography technology is indispensable in order to pattern the workpiece containing conducting films, such as insulator layers, such as a silicon oxide film, a silicon nitride film, etc. which were formed on the semiconductor substrate, or an aluminum alloy film, and a copper alloy film, or the semiconductor substrate itself after desired shape. After applying on a workpiece using the photoresist exposed to ultraviolet rays and forming a photoresist film from the former in this photo lithography, this photoresist film is irradiated with ultraviolet rays via a mask pattern (exposure), Deteriorating a UV irradiation field in solubilization (positive type), and deteriorating a UV irradiation field in insolubilization (negative mold) is performed. Next, after carrying out the development of the photoresist film, and a solvent's removing a solubilization field selectively and forming a resist pattern, he makes a workpiece etch selectively and is trying and to pattern it by using this resist pattern as a mask.

[0003]Here, generally as a material of above-mentioned photoresist, the novolac system photoresist of the positive type is used from the former. Since the photoresist of a positive type has the feature that resolution is excellent as compared with it of a negative mold, as for most this kind of photoresist, the positive type is used. On the other hand, although

ultraviolet rays, such as g line (438 nm of wavelength abbreviation) and i line (365 nm of wavelength abbreviation), were used as exposing light of photoresist. In order to obtain a more precise resist pattern, the photo lithography which makes exposing light the far ultraviolet ray which comprises a KrF (krypton fluoridation) excimer laser beam (248 nm of wavelength abbreviation) is realized.

[0004]By the way, along with improvement in integration of LSI, the photo lithography in which micro processing is more possible comes to be required, and in connection with this, the exposing light of photoresist is going in the direction using the ultraviolet rays of short wavelength rather than high resolution is obtained. As a result, for manufacture of DRAM (Dynamic Random Access Memory) with the degree of location beyond 1G bit which needs 0.18 micrometer or less of especially processing technology. [Donald C. Hoffer et al. use of the photo lithography using the ArF (argon fluoridation) excimer laser beam (193 nm of wavelength abbreviation) which generates the far ultraviolet ray whose wavelength is shorter than an above-mentioned KrF excimer laser light is considered to be these days, Journal of Photopolymer Science and Technology (Journal of Photopolymer Science and Technology), nine volumes (No. 3), 387page-397page(1996)].

[0005]However, since novolac system photoresist has the character in which optical absorption is large when the above-mentioned conventional novolac system photoresist is exposed by above-mentioned ArF excimer laser light, it becomes difficult to obtain a good resist pattern. So, development of resin for resist corresponding to the photo lithography using ArF excimer laser light is desired. On the occasion of development of this resin for resist for ArF excimer laser light, it is necessary to fill improvement in the cost performance of laser from the life of the gas which is a raw material of laser being short, and the laser device itself being expensive, and there being etc. For this reason, in addition to the high resolution nature corresponding to the minuteness making of a working dimension, the demand to high-sensitivity-izing is high.

[0006]The chemical amplification type resist which used the photo-oxide generating agent which is a sensitizing agent as the method of high-sensitivity-izing of resin for resist is known well, for example, it is indicated to JP,2-27660,B. The resist which becomes the gazette from the combination of triphenylsulfonium hexafluoroacetate and poly (p-tert-butoxycarbonyloxy alpha-methylstyrene) is indicated. Such chemical amplification type resist is widely used for the resist for KrF excimer lasers now [for example, Hiroshi Ito, C. GURANTOU Hirson, American Chemical Society Symposium Series 242 volume, and 11 pages - 23 pages (1984)]. The feature of chemical amplification type resist is that the proton acid by which it was generated by optical exposure starts resist resin etc. and an acid catalyzed reaction from the photo-oxide generating agent which is a component by heat-treatment after exposure. Thus, photoreaction efficiency (reaction per one photon) has attained fast high sensitivity-ization compared with less than one conventional resist. The great portion of resist developed now is a chemical amplification type.

[0007]In however, the case of the lithography using the far ultraviolet ray of the wavelength not more than abbreviated 220nm represented by ArF excimer laser light. The new characteristic cannot be satisfied with the conventional material of the characteristic, i.e., the high transparency and dry etching resistance over exposing light of wavelength not more than abbreviated 220nm, is needed for the resist for forming a minute pattern. The conventional g line (438 nm of wavelength abbreviation) mentioned

above here, i line (365 nm of wavelength abbreviation), KrF excimer laser light (248 nm of wavelength abbreviation) -- the resin which has an aromatic ring mainly being used into structural units, such as novolak resin or poly (p-vinylphenol), as a resinous principle, and resin for photoresist of business, The etching resistance of resin has been maintained by the dry etching resistance of this aromatic ring. However, the resin which has an aromatic ring has the very strong optical absorption to the light of the wavelength not more than abbreviated 220nm. Therefore, since a great portion of exposing light is absorbed in a resist surface and exposing light does not penetrate even a substrate, formation of a detailed resist pattern cannot be performed. For this reason, resin is conventionally inapplicable to the photo lithography using the far ultraviolet ray of 220 nm or less of abbreviation as it is. Therefore, it has etching resistance, excluding an aromatic ring, and is anxious for transparent resin for resist to the far ultraviolet ray of the wavelength not more than abbreviated 220nm.

[0008]As a high molecular compound which has transparency to ArF excimer laser light (193 nm of wavelength abbreviation), and moreover has dry etching resistance, Copolymer [Takechi et al. with the adamantyl methacrylate unit which is alicycle fellows polymers, Journal of Photopolymer Science and Technology (Journal of Photopolymer Science and Technology), Five volumes (No. 3), 439 pages - 446 page (1992)], and copolymer [R. with an isobornyl methacrylate unit D. allenes (R. D.Allen), Journal of Photopolymer Science and Technology (Journal of Photopolymer Science and Technology), Eight volumes (No. 4), 623 pages - 636 pages (1995) and nine volumes (No. 3), and 465 pages - 474 page (1996)] (the former is called hereafter) are proposed. [0009]Resin [F. with the alternating copolymerization unit of norbornene and a maleic anhydride M. HORIHAN et al. (F. M.Houlihan), Macro leakage-at-bulb KYURUZU (Macromolecules), 30 volumes, and 6517 -6524-page (1997)] (the latter is called hereafter) are proposed.

[0010]

[Problem(s) to be Solved by the Invention]By the way, a fault which is explained below, respectively exists in resin for resist corresponding to the lithography using the far ultraviolet ray of the wavelength not more than abbreviated 220nm represented by the above-mentioned conventional ArF excimer laser light.

[0011]First, the acrylate derivative which has the alicycle group used in the former resin (meta) does not have the polar groups (for example, a carboxyl group, hydroxyl, etc.) which have substrate adhesion. For this reason, it is difficult for hydrophobicity to be strong, and for adhesion with a processing substrate (for example, silicon substrate) to be bad, and to form a uniform coating film with sufficient reproducibility in the homopolymer of the monomer which has an alicycle group. Since it does not have the adamantane content residue which furthermore has dry etching resistance, isoBONIRU content residue, or the residue which may reveal the solubility difference in exposure order in a menthyl content residue unit, a pattern cannot be formed by exposure. Therefore, by former resin, it will not be able to use without considering it as a copolymerization-ized object with the comonomer which can demonstrate solubility differences, such as t \*\*BUCHIRU methacrylate and tetrahydro methacrylate, or comonomer with substrate adhesion like methacrylic acid as a resinous principle of resist. However, it is abbreviation 50 mol % necessity, and since the dry etching resistance of a comonomer unit is remarkable and comonomer content has it, the dry-etching-resistance

effect by an alicycle group falls remarkably, and it is deficient in it to the practicality as dry-etching-resistance resin. [ low ]

[0012]Next, also in resin using the latter above-mentioned norbornene and the alternating copolymer of the maleic anhydride, since it does not have a polar group in a norbornane ring, adhesion is low. Therefore, in resin with the alternating copolymerization unit of norbornene and a maleic anhydride, the copolymer with acrylic acid with substrate adhesion, etc. is used, and, as a result, practicality is low as dry-etching-resistance resin. For this reason, the optical transparency over the far ultraviolet ray of the wavelength not more than abbreviated 220nm is high, and etching resistance is high, and it is anxious for the new positive type chemical amplification resist which was excellent in substrate adhesion.

[0013]This invention was made in view of the above-mentioned situation, its optical transparency over the far ultraviolet ray of the wavelength not more than abbreviated 220nm is high, and its etching resistance is high, and an object of an invention is to provide resin for resist and chemical amplification type resist which were excellent in substrate adhesion, and the pattern formation method using it.

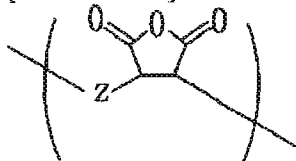
[0014]

[Means for Solving the Problem]In order to solve an aforementioned problem, the invention according to claim 1 relates to resin for resist in which an acidolysis nature group decomposes by operation of acid, and solubility to an alkaline aqueous solution increases, and is characterized by having alicyclic lactone structure in a main chain.

[0015]The invention according to claim 2 relates to the resin for resist according to claim 1, and is characterized by expressing the above-mentioned alicyclic lactone structure with a general formula (10).

[0016]

[Formula 10]



(10) (in an upper type, Z is an alicyclic hydrocarbon group which has lactone structure.)

[0017]The invention according to claim 3 relates to the resin for resist according to claim 1, and is characterized by expressing the above-mentioned alicyclic lactone structure with a general formula (11).

[0018]

[Formula 11]

(11) (in an upper type, Z is an alicyclic hydrocarbon group which has lactone structure.)

[0019]The invention according to claim 4 relates to the resin for resist according to claim 1, and is characterized by expressing the above-mentioned alicyclic lactone structure with a general formula (12).

[0020]

[Formula 12]



(12) (in an upper type, q is a positive integer of 0, or 1-3, and r is 1 or 2.)

[0021]The invention according to claim 5 relates to the resin for resist according to claim 1, and is characterized by expressing the above-mentioned alicyclic lactone structure with a general formula (13).

[0022]

[Formula 13]

(13) (in an upper type, R is an alkyl group of the carbon numbers 1-4, and w is a positive integer of 1-3.)

[0023]The invention according to claim 6 relates to the resin for resist according to claim 1, and is characterized by expressing with a general formula (14) the resin which has alicyclic lactone structure in the above-mentioned main chain.

[0024]

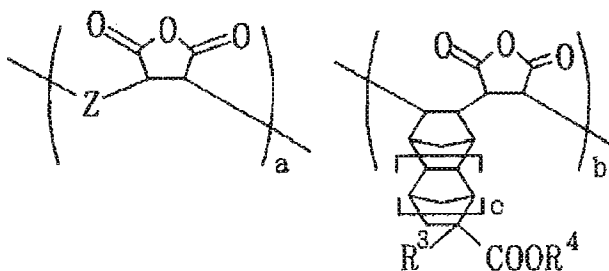
[Formula 14]

(14) (in an upper type, the alicyclic hydrocarbon group with which Z has lactone structure, and  $R^1$  express the bridged cyclic hydrocarbon group of the carbon numbers 7-13 which have a hydrogen atom or a methyl group, a basis that decomposes  $R^2$  with acid, or a basis decomposed with acid.) x and y are arbitrary numbers which fill  $x+y=1$ ,  $0 < x < 1$ , and  $0 < y < 1$ , respectively.

[0025]The invention according to claim 7 relates to the resin for resist according to claim 1, and is characterized by expressing with a general formula (15) the resin which has alicyclic lactone structure in the above-mentioned main chain.

[0026]

[Formula 15]

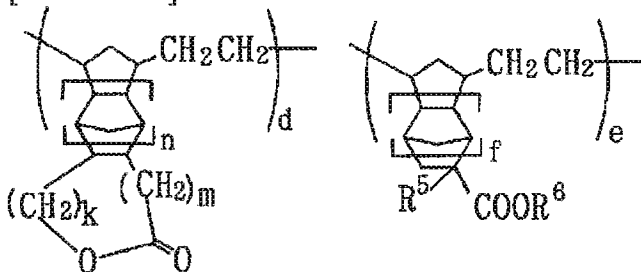


(15) (in an upper type, the alicyclic hydrocarbon group with which Z has lactone structure, and  $R^3$  express a hydrogen atom or a methyl group, and the basis that decomposes  $R^4$  with acid.) a and b are arbitrary numbers which fill  $a+b=1$ ,  $0 < a < 1$ , and  $0 < b < 1$ , respectively. c is 0 or 1.

[0027] The invention according to claim 8 relates to the resin for resist according to claim 1, and is characterized by expressing with a general formula (16) resin which has alicyclic lactone structure in the above-mentioned main chain.

[0028]

[Formula 16]

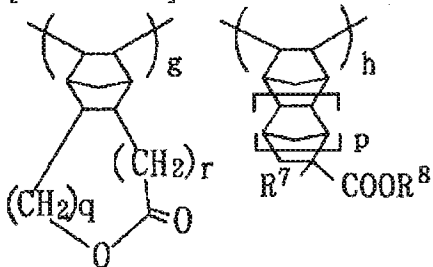


(16) (in an upper type, 0 or 1, and  $R^5$  express the basis into which the positive integer of 0, or 1-3 decomposes k into, and, as for m, 0 or 1 or 2n, and f decompose a hydrogen atom or a methyl group, and  $R^6$  with acid, respectively.) d and e are arbitrary numbers which fill  $d+e=1$ ,  $0 < d < 1$ , and  $0 < e < 1$ , respectively.

[0029] The invention according to claim 9 relates to the resin for resist according to claim 1, and is characterized by expressing with a general formula (17) the resin which has alicyclic lactone structure in the above-mentioned main chain.

[0030]

[Formula 17]



(17) In [top type, 0 or 1 (however, p is 1 when r is 0.), and  $R^7$  express a basis into which a positive integer of 0, or 1-3 decomposes q into, and, as for r, 0, or 1 or 2p decomposes a hydrogen atom or a methyl group, and  $R^8$  with acid. g and h are arbitrary numbers which fill  $g+h=1$ ,  $0 < g < 1$ , and  $0 < h < 1$ , respectively. ]

[0031]The invention according to claim 10 relates to the resin for resist according to claim 1, and is characterized by expressing with a general formula (18) resin which has alicyclic lactone structure in the above-mentioned main chain.

[0032]

[Formula 18]

(18) (in an upper type, the basis into which w decomposes R into by the alkyl group of the carbon numbers 1-4, the positive integer of 1-3 decomposes it into, and, as for w1, 0 or 1, and R<sup>10</sup> decompose a hydrogen atom or a methyl group, and R<sup>11</sup> with acid is expressed.) x1 and y1 are arbitrary numbers which fill x1+y1=1, 0<x1<1, and 0<y1<1, respectively.

[0033]The invention according to claim 11 relates to chemical amplification type resist, and is characterized by being the positive type chemical amplification resist which contains at least a photo-oxide generating agent which generates acid by resin for resist according to any one of claims 1 to 10 and exposure.

[0034]A process of the invention according to claim 12 starting a pattern formation method, and applying the chemical amplification type resist according to claim 11 on a processing substrate, It is characterized by including a process of exposing the above-mentioned processing substrate with light with a wavelength of 180-220 nm, a process of carrying out bake of the above-mentioned processing substrate, and a process of developing the above-mentioned processing substrate.

[0035]The invention according to claim 13 relates to the pattern formation method according to claim 12, and is characterized by the above-mentioned exposing light being ArF excimer laser light.

[0036]

[Embodiment of the Invention]In advance of explanation of the embodiment of the invention of \*\*\*\*\*, the premise of this invention is explained roughly. The artificer of this invention completed this invention, as a result of inquiring wholeheartedly to achieve the above objects. This invention has a basic feature in the resin for resist which has alicyclic lactone structure in a main chain, and the pattern formation method using the chemical amplification type resist and it which contain this resin for resist further has the feature.

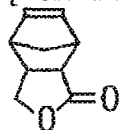
[0037]The resin which has a structural unit expressed with general formula (1) - (4) as resin for resist which has alicyclic lactone structure is mentioned to an above-mentioned main chain. These general formulas (1) Although the resin expressed with general formula (5) - (9) is mentioned as a concrete example of the resin which has a structural unit expressed with - (4), it is not limited only to these. May also include the structural unit which can carry out copolymerization to the resin expressed with general formula (5) - (9) further, and as other vinyl monomers which can carry out copolymerization, For example, aliphatic series ester of acrylic acid (meta), such as acrylic acid (meta), methyl acrylate (meta), and ethyl acrylate (meta), Adamanthy (meta) acrylate, tricyclo decyl

(meta) acrylate, Tetracyclo dodecyl (meta) acrylate, norbornyl (meta) acrylate, Alicyclic ester of acrylic acid (meta), such as isobornyl (meta) acrylate, The acrylate derivative which has a lactone structure given in JP,2000-26446,A (meta), The norbornene derivative containing a carboxyl group, hydroxyl, etc. for example, a 5-norbornene 2-oar and 5-norbornene 2 \*\*META Norian. the tetracyclo dodecyl derivative (3-tetracyclo [-- 4.4.0. -- <sup>12, 5, 1<sup>7</sup>, and 10</sup>] dodecen 8 \*\*KARUBON acid.) containing carboxyl groups, hydroxyls, etc., such as 5-norbornene 2-carboxylic acid 3-tetracyclo [4.4.0.1<sup>2, 5, 1<sup>7, 10</sup></sup>] dodecen 8 \*\*ORU, Although 3-tetracyclo [4.4.0.1<sup>2, 5, 1<sup>7, 10</sup></sup>] dodecen 8 \*\*META Norian, itaconic acid anhydride, etc. are mentioned, it is not limited only to these. the weight average molecular weight of resin -- 2000-200000 -- it is 3000-100000 preferably. [0038]Although it has an alicyclic hydrocarbon group which has lactone structure in a main chain to resin for resist of an invention, the feature is in lactone structure. Generally, lactone structure has high specific inductive capacity compared with ester structure, ether structure, and alcohol structure (for example, if the compound of the carbon number 4 compares). Specific inductive capacity of gamma-butyrolactone: Indicate to 39, ethyl acetate:6.02, diethylether:4.335, an 1-butanol:17.51 chemicals manual, the basic volume 2, the 3rd edition of revision, etc. As a result, polarity becomes high and, as for the resin which has an alicyclic lactone skeleton in a main chain, the resist using resin of this invention has the feature that the adhesion over a substrate is also very good. Furthermore, to resin of this invention, since it has not only lactone structure but an alicyclic hydrocarbon group, it also has the feature that the dry etching resistance of resin is excellent.

[0039]And the norbornene derivative with the lactone structure which is one of the raw materials used for composition of resin and which is expressed with a formula (19) is compounded by the following methods, for example.

[0040]

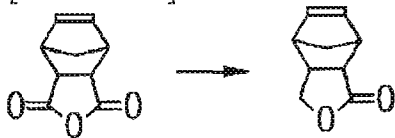
[Formula 19]



(19) Namely, it applies to a method of J.Org.Chem.35 volume, D.M.Bailey and others indicated to 3574 - 3576 pages (1970) correspondingly, 5-norbornene endo-2, 3-dicarboxylic anhydride or 5-norbornene exo-2, and 3-dicarboxylic anhydride (W. -- Heitz et al.) It is compounded by returning Macromol.Chem.Phys., 200 volumes, and 338 - 347 pages (1999) with sodium borohydride (NaBH<sub>4</sub>) among a tetrahydrofuran. (20) types shown below are the reaction formula.

[0041]

[Formula 20]



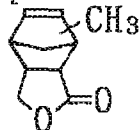
(20)

[0042]The norbornene derivative with the lactone structure expressed with a formula (21)

is compounded by the following methods, for example.

[0043]

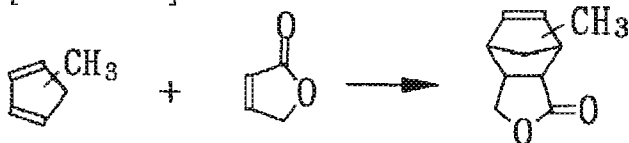
[Formula 21]



(21) Namely, it applies to a method of J.Org.Chem.35 volume, D.M.Bailey and others indicated to 3574 - 3576 pages (1970) correspondingly, It is compounded by returning a methyl-5-norbornene endo-2,3-dicarboxylic anhydride or a methyl-5-norbornene exo-2,3-dicarboxylic anhydride with sodium borohydride ( $\text{NaBH}_4$ ) among a tetrahydrofuran. It is compounded as other methods by the Diels-Alder (Diels-Alder) reaction of methylcyclopentadiene and 2(5H)-furan obtained by a pyrolysis of a methylcyclopentadiene dimer. (22) types shown below are the reaction formula.

[0044]

[Formula 22]



(22) Resin expressed with a general formula (5) is compounded, for example by the following methods. Namely, a maleic anhydride and an alicyclic olefin which has lactone structure. (For example, a norbornene derivative with lactone structure expressed with formula (19)), An acrylate derivative (for example, t-butoxycarbonyltetracyclododecylacrylate) which has an acidolysis nature group (meta) Inside of a dry tetrahydrofuran, 60-65 °C is compounded by making it react for 2 to 24 hours under radical polymerization initiator existence, such as azobisisobutyronitrile. Resin expressed with a general formula (6) is compounded, for example by the following methods. Namely, a maleic anhydride and an alicyclic olefin which has lactone structure. (For example, a norbornene derivative with lactone structure expressed with formula (19)), It is compounded by making 60-65 °C of alicyclic olefin derivatives (for example, 5-norbornene 2-carboxylic acid t-butylester) which have an acidolysis nature group react under radical polymerization initiator existence, such as azobisisobutyronitrile, among a dry tetrahydrofuran for 2 to 24 hours.

[0045] Resin expressed with a general formula (7) is compounded, for example by the following methods. Namely, an alicyclic olefin (for example, norbornene derivative with lactone structure expressed with a formula (19)) which has lactone structure and an alicyclic olefin derivative which has an acidolysis nature group. (for example, 3-tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>] dodecen 8-yl t-butyl ester) -- metathesis catalyst [-- for example, A halogenide of transition metals, such as W (tungsten), Mo (molybdenum), and Re (rhenium), etc. (For example, although  $\text{WCl}_6$ ,  $\text{MoCl}_5$ ,  $\text{ReCl}_3$ , etc. are mentioned, it is not limited only to these) Ring opening polymerization is carried out using], and it is compounded by hydrogenating using precious metal catalysts, such as palladium, further.

[0046] Resin expressed with a general formula (8) is compounded, for example by the

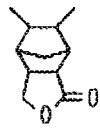
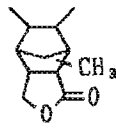
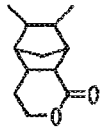
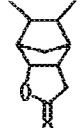
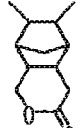
following methods. namely, alicyclic olefin [which has lactone structure, for example, 5,8-methano-3,4,4 a,5,8,8a-hexahydro,3H-2-benzopyran 3-one (H. -- Shimomura et al..) Tetrahedron Lett., No.45, 4099 -4102-page (1976)], and 5-norbornene 2 \*\*KARUBON acid t-butylester, It applies to a method of J.P.Mathew and others Macromolecules, 29 volumes, and given in 2755 -2763 page (1996) correspondingly, It is compounded by making palladium compounds (for example,  $\{(\eta^3\text{-allyl}) \text{Pd} (\text{BF}_4)\}$ ,  $[\text{Pd}(\text{CH}_3 \text{CN})_4]$ , and  $[\text{BF}_4]_2$  etc.) into a catalyst, and carrying out addition condensation.

[0047]Resin expressed with a general formula (9) is compounded, for example by the following methods. Namely, an alicyclic olefin (for example, norbornene derivative with lactone structure expressed with a formula (21)) and 3-tetracyclo dodecen 8

\*\*KARUBON acid t-butylester which have lactone structure, It applies to a method of J.P.Mathew and others Macromolecules, 29 volumes, and given in 2755 -2763 page (1996) correspondingly, It is compounded by making palladium compounds (for example,  $\{(\eta^3\text{-allyl}) \text{Pd} (\text{BF}_4)\}$ ,  $[\text{Pd}(\text{CH}_3 \text{CN})_4]$ , and  $[\text{BF}_4]_2$  etc.) into a catalyst, and carrying out addition condensation. A general formula (1) and general formula (2) Set, and Z is lactone structure an alicyclic hydrocarbon group which it has, and a concrete example, A norbornane derivative which has the lactone structure shown in Table 1 and 2, a tetracyclo [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>] dodecane derivative which has lactone structure, Although a cyclopentane derivative which has lactone structure, a tricyclodecane derivative which has lactone structure, etc. are mentioned, it is not limited only to them.

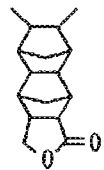
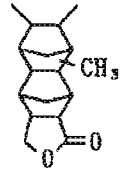
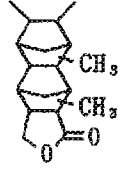
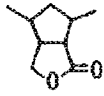
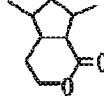
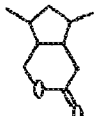
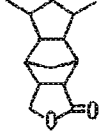
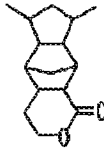
[0048]

[Table 1]

	Zの化学構造
ラクトン構造を持つ ノルボルナン誘導体(1)	
ラクトン構造を持つ ノルボルナン誘導体(2)	
ラクトン構造を持つ ノルボルナン誘導体(3)	
ラクトン構造を持つ ノルボルナン誘導体(4)	
ラクトン構造を持つ ノルボルナン誘導体(5)	

[0049]

[Table 2]

ラクトン構造を持つ テトラシクロ [4.4.0.1 <sup>2,5</sup> .1 <sup>7,10</sup> ] ドデカン誘導体(1)	
ラクトン構造を持つ テトラシクロ [4.4.0.1 <sup>2,5</sup> .1 <sup>7,10</sup> ] ドデカン誘導体(2)	
ラクトン構造を持つ テトラシクロ [4.4.0.1 <sup>2,5</sup> .1 <sup>7,10</sup> ] ドデカン誘導体(3)	
ラクトン構造を持つ シクロペンタン誘導体(1)	
ラクトン構造を持つ シクロペンタン誘導体(2)	
ラクトン構造を持つ シクロペンタン誘導体(3)	
ラクトン構造を持つ トリシクロデカン誘導体(1)	
ラクトン構造を持つ トリシクロデカン誘導体(2)	

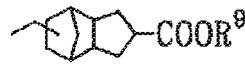
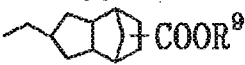
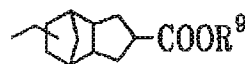

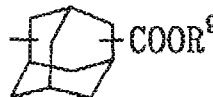
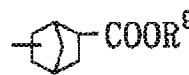
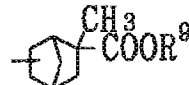
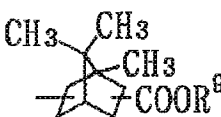


In a general formula (3), q is a positive integer of 0, or 1-3, and r is 1 or 2. In a general formula (4), R<sup>1</sup> is a hydrogen atom or a methyl group in a general formula (5) whose R is

an alkyl group (they are specifically a methyl group, an ethyl group, a propyl group, and a butyl group.) of the carbon numbers 1-4 and whose  $w$  is a positive integer of 1-3. A concrete example of a basis which  $R^2$  is a bridged cyclic hydrocarbon group of the carbon numbers 7-13 which have a basis decomposed with acid, or a basis decomposed with acid, and is decomposed with acid, t-butyl group, a tetrahydropyran 2 \*\*IRU group, a tetrahydrofuran 2 \*\*IRU group, A 4-methoxytetrahydropyran 4 \*\*IRU group, 1-ethoxyethyl group, 1-butoxyethyl group, 1-propoxyethyl group, a 3-oxocyclohexyl group, A 2-methyl-2-adamantyl group, a 2-ethyl-2-adamantyl group, An 8-methyl-8-tricyclo [5.2.1.0<sup>2,6</sup>] decyl group, Or although a 1,2,7,7-tetramethyl 2-norbornyl group, 2-acetoxymenthyl group, 2-hydroxy menthyl group, a 1-methyl-1-cyclohexylethyl group, etc. are mentioned, it is not limited only to these. A concrete example of a bridged cyclic hydrocarbon group of the carbon numbers 7-13 which have a basis decomposed with acid, 5.2.1.0<sup>2, tricyclo [6]</sup> decylmethyl group which have an ester group as shown in Table 3, A tricyclo [5.2.1.0<sup>2,6</sup>] decyl group, an adamantyl group, Although a norbornyl group, a methyl norbornyl group, an isobornyl group, tetracyclo [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>] dodecyl, methyltetracyclo [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>] dodecyl, etc. are mentioned, It is not limited only to these (however,  $R^9$  in Table 3 is a basis decomposed with acid, and a concrete example). t-butyl group, a tetrahydropyran 2 \*\*IRU group, a tetrahydrofuran 2 \*\*IRU group, A 4-methoxytetrahydropyran 4 \*\*IRU group, 1-ethoxyethyl group, 1-butoxyethyl group, 1-propoxyethyl group, a 3-oxocyclohexyl group, A 2-methyl-2-adamantyl group, 2-ethyl-2-adamantyl group, 3-hydroxy-1-adamantyl group, 8-methyl-8-tricyclo [5.2.1.0<sup>2,6</sup>] decyl group or 1, 2 and 7, and 7-tetramethyl 2-norbornyl group, Although 2-acetoxymenthyl group, 2-hydroxy menthyl group, a 1-methyl-1-cyclohexylethyl group, etc. are mentioned, it is not limited only to these. . Although the rate  $x$  of a unit of having alicyclic lactone structure is  $0 < x < 1$ , from points, such as the definition of resist, and substrate adhesion,  $0.1 < x < 0.8$  is more preferred.

[0050]

[Table 3]



	基の化学構造
エステル基を持つ トリシクロ [5.2.1.0 <sup>2,6</sup> ] デシルメチル基	 or 
エステル基を持つ トリシクロ [5.2.1.0 <sup>2,6</sup> ] デシル基	 or 
エステル基を持つ アダマンチル基	
エステル基を持つ ノルボルニル基	
エステル基を持つ メチルノルボルニル基	
エステル基を持つ イソボルニル基	
エステル基を持つ テトラシクロ [4.4.0.1 <sup>2,5</sup> .1 <sup>7,10</sup> ] ドデシル基	
エステル基を持つメチル テトラシクロ [4.4.0.1 <sup>2,5</sup> .1 <sup>7,10</sup> ] ドデシル基	

[0051] In a general formula (6), 0 or 1, and R<sup>3</sup> of c are a hydrogen atom or a methyl group. The concrete example of the basis which R<sup>4</sup> is a basis decomposed with acid and is decomposed with acid, t-butyl group, a tetrahydropyran 2 \*\*IRU group, a tetrahydrofuran 2 \*\*IRU group, A 4-methoxytetrahydropyran 4 \*\*IRU group, 1-ethoxyethyl group, 1-butoxyethyl group, 1-propoxyethyl group, a 3-oxocyclohexyl group, A 2-methyl-2-adamantyl group, a 2-ethyl-2-adamantyl group, An 8-methyl-8-tricyclo [5.2.1.0<sup>2,6</sup>] decyl group, Or although a 1,2,7,7-tetramethyl 2-norbornyl group, 2-acetoxy menthyl group, 2-hydroxy menthyl group, a 1-methyl-1-cyclohexylethyl group, etc. are mentioned, it is not limited only to these. Although the rate a of a unit of having alicyclic lactone structure is 0 < a < 1, from points, such as the definition of resist, and substrate

adhesion,  $0.1 < a < 0.8$  is more preferred.

[0052] The resin expressed with a general formula (6) has  $c$  more preferred than 0 among a formula from the dry etching resistance point that the resin which is 1 is [ the carbon density of resin ] more expensive. In a general formula (7), the positive integer of 0, or 1-3 and  $m \geq 0$ , or 1 or  $2n$ . The concrete example of the basis which 0 or 1, and  $R^5$  are a hydrogen atom or a methyl group, and a basis that decomposes  $R^6$  with acid, and  $f$  decomposes with acid, respectively, *t*-butyl group, a tetrahydropyran 2 \*\*IRU group, a tetrahydrofuran 2 \*\*IRU group, A 4-methoxytetrahydropyran 4 \*\*IRU group, 1-ethoxyethyl group, 1-butoxyethyl group, 1-propoxyethyl group, a 3-oxocyclohexyl group, A 2-methyl-2-adamantyl group, a 2-ethyl-2-adamantyl group, An 8-methyl-8-tricyclo [5.2.1.0<sup>2,6</sup>] decyl group, Or although a 1,2,7,7-tetramethyl 2-norbornyl group, 2-acetoxy menthyl group, 2-hydroxy menthyl group, a 1-methyl-1-cyclohexylethyl group, etc. are mentioned, it is not limited only to these. Although the rate  $d$  of a unit of having alicyclic lactone structure is  $0 < d < 1$ , from points, such as the definition of resist, and substrate adhesion,  $0.1 < d < 0.8$  is more preferred.

[0053] The resin expressed with a general formula (7) has  $n$  and  $f$  more preferred than 0 among a formula from the dry etching resistance point that the resin which is 1 is [ the carbon density of resin ] more expensive. In a general formula (8), as for  $q$ , 0, or 1 or  $2p$  the positive integer of 0, or 1-3, and  $r$  0 or 1. (however,  $p$  is 1 when  $r$  is 0.) -- a hydrogen atom or a methyl group, and  $R^6$  are bases decomposed with acid, and  $R^7$  the concrete example of the basis decomposed with acid, *t*-butyl group, a tetrahydropyran 2 \*\*IRU group, a tetrahydrofuran 2 \*\*IRU group, A 4-methoxytetrahydropyran 4 \*\*IRU group, 1-ethoxyethyl group, 1-butoxyethyl group, 1-propoxyethyl group, a 3-oxocyclohexyl group, A 2-methyl-2-adamantyl group, a 2-ethyl-2-adamantyl group, An 8-methyl-8-tricyclo [5.2.1.0<sup>2,6</sup>] decyl group, Or although a 1,2,7,7-tetramethyl 2-norbornyl group, 2-acetoxy menthyl group, 2-hydroxy menthyl group, a 1-methyl-1-cyclohexylethyl group, etc. are mentioned, it is not limited only to these. Although the rate  $g$  of a unit of having alicyclic lactone structure is  $0 < g < 1$ , from points, such as the definition of resist, and substrate adhesion,  $0.1 < g < 0.8$  is more preferred.

[0054] The resin expressed with a general formula (8) has  $p$  more preferred than 0 among a formula from the dry etching resistance point that the resin which is 1 is [ the carbon density of resin ] more expensive.  $R$  in a general formula (9) The alkyl group of the carbon numbers 1-4. (specifically, they are a methyl group, an ethyl group, a propyl group, and a butyl group.). A hydrogen atom or a methyl group, and  $R^{11}$  are bases into which the positive integer of 1-3 decomposes  $w$  into, and 0 or 1, and  $R^{10}$  decompose  $w$  with acid, and the concrete example of the basis decomposed with acid, *t*-butyl group, a tetrahydropyran 2 \*\*IRU group, a tetrahydrofuran 2 \*\*IRU group, A 4-methoxytetrahydropyran 4 \*\*IRU group, 1-ethoxyethyl group, 1-butoxyethyl group, 1-propoxyethyl group, a 3-oxocyclohexyl group, A 2-methyl-2-adamantyl group, a 2-ethyl-2-adamantyl group, An 8-methyl-8-tricyclo [5.2.1.0<sup>2,6</sup>] decyl group, Or although a 1,2,7,7-tetramethyl 2-norbornyl group, 2-acetoxy menthyl group, 2-hydroxy menthyl group, a 1-methyl-1-cyclohexylethyl group, etc. are mentioned, it is not limited only to these. Although the rate  $x$  of a unit of having alicyclic lactone structure is  $0 < x < 1$ , from points, such as the definition of resist, and substrate adhesion,  $0.1 < x < 0.8$  is more preferred. Among the formula, since the resin expressed with a general formula (9) has an alkyl group expressed with  $R$ , compared with resin without an alkyl group, the carbon

density of resin becomes high and it is excellent from the dry etching resistance point. [0055]and the weight average molecular weight of resin for resist of this invention -- 2000-200000 -- it is 3000-100000 preferably. It is because formation of a resist film is easy for it in a molecular weight being 2000 or more, and it excels that it is 200000 or less in the solubility to the solvent of resin and excels also in resolution characteristics. The positive type chemical amplification resist of this invention makes the main constituents resin, a photo-oxide generating agent, and the solvent that dissolves these, and the content of the inside of all the constituent 100 weight sections and resin excluding a solvent is usually preferably good to consider it as 70 to 99 weight section 60 to 99.8 weight section. As for the photo-oxide generating agent used for this invention, it is preferably desirable that it is a photo-oxide generating agent which generates acid by the optical exposure of the range of 180 nm - 220 nm 400 nm or less, A mixture with the high molecular compound in this invention moreover shown previously, etc. may fully dissolve in an organic solvent, and by the producing-film methods, such as a spin coat, as long as a uniform coating film can be formed, what kind of photo-oxide generating agent may be sufficient as that solution. It may be independent, or two or more sorts may be mixed and used.

[0056]As an example of an usable photo-oxide generating agent, for example 43 journal OBU JI organic chemistry (Journal of the Organic Chemistry), No. 15, the triphenylsulfonium salt derivative of J.V. Crivello and others (J. V.Crivello) indicated to 3055 pages - 3058 pages (1978), and other onium salt (for example, sulfonium salt.) represented by it Compounds, such as iodonium salt, phosphonium salt, diazonium salt, and ammonium salt, 2 and 6-dinitro benzyl ester [O. Nalamasu et al. (O. Nalamasu), A SPIE proceeding, 1262 volumes, 32page(1990)], 1, 2, 3-Tri (methane sulfonyloxy) benzene [Takumi Ueno et al., There are alkyl sulfonium salt etc. which were indicated in 89, Kodansha, 413-424page(1990)], the sulfo Succin imide indicated by JP,5-134416,A \*\*\*\*\* , and the proceeding OBU and PME' patent No. 2964990 gazette.

[0057]The content of a photo-oxide generating agent is usually one to 15 weight section preferably 0.2 to 30 weight section among all [ excluding the solvent contained in positive type chemical amplification resist ] constituent 100 weight section. Sensitivity with this content sufficient by 0.2 or more weight sections is obtained, and formation of a pattern becomes easy. Formation of a uniform coating film becomes it easy that they are 30 or less weight sections, and it becomes further difficult to generate a residue (SCUM) after development.

[0058]It adds to resin, a photo-oxide generating agent, etc., and optimum dose of solvents are contained in the positive type chemical amplification resist of this invention. As long as it can dissolve uniformly the ingredient which consists of resin and a photo-oxide generating agent and a uniform coating film can be formed by methods, such as a spin coat method, using that resist, what kind of organic solvent may be sufficient as this solvent. One kind of organic solvent may be independently used for a solvent, and two or more kinds may be mixed and used. Specifically N-propyl alcohol, isopropyl alcohol, n-butyl alcohol, Alcohols, such as tert-butyl alcohol, methyl-cellosolve acetate, Ethylcellosolve acetate, propylene glycol monoethyl ether acetate, Methyl lactate, ethyl lactate, acetic acid 2-methoxy butyl, 2-ethoxyethyl acetate, Methyl pyruvate, ethyl pyruvate, 3-methoxy methyl propionate, Ester species, such as 3-methoxy ethyl propionate, N-methyl-2-pyrrolidinone, Cyclic ketone alcohols, such as cyclohexanone,

cyclopentanone, and cyclohexanol, Ketone, such as methyl ethyl ketone, 1,4-dioxane, ethylene glycol monomethyl ether, Ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether, Although glycol ether, such as ethylene glycol monoisopropyl ether, diethylene glycol monomethyl ether, and diethylene glycol dimethyl ether, is mentioned as an example of a desirable solvent, of course, it is not limited only to these. [0059]Although the "fundamental" constituents of the positive resist of this invention are the above-mentioned resin, a photo-oxide generating agent, and a solvent, they may add other ingredients, such as a lysis inhibition agent, an organic base, a surface-active agent, coloring matter, stabilizer, a spreading nature improving agent, and a color, if needed. The pattern formation method of this invention is the method of carrying out transfer formation of the mask pattern on a resist application film using the exposing light chosen as exposure of resist from the range of 180-220-nm wavelength using the positive type chemical amplification resist of this above-mentioned invention. In this process, each process of a resist application, the baking treatment before exposure, the baking treatment after exposure, and development is intrinsically [ as the pattern formation which uses the conventional chemical amplification type resist ] the same.

[0060]Hereafter, this embodiment of the invention is described based on an above-mentioned premise. Explanation is concretely given using an example.

<> The norbornene derivative expressed with the example type of the 1st composition (10) (Endo object)

The sodium borohydride 12.8g is added to 100 ml of tetrahydrofurans (it abbreviates to THF hereafter), What dissolved 50 g of 5-norbornene endo-2 and 3-dicarboxylic anhydrides (the Wako Pure Chem make, product number 146-03435) in THF200ml is dropped there under ice-cooling. After agitating at a room temperature for 3 hours, 150 ml of 6N chloride is added under ice-cooling, and it agitates at a room temperature further for 3 hours. A \*\* exception carries out precipitate which deposits and a filtrate is condensed under decompression. 300 ml of chloroform is added to residue, silica gel is added further, and adsorption treatment of the impurity is carried out. And 16.5g of objects were obtained by distilling off chloroform under decompression (36% of yield). <sup>1</sup>H-NMR(CDCl<sub>3</sub>):delta(ppm)1.47 (1H, dd), 1.65 (1H, d), 3.06-3.15 (2H, m), 3.26-3.28 (1H, m), 3.32-3.36 (1H, m), 3.8 (1H, dd), 4.29 (1H, t), 6.3 (2H, s).

[0061]<> The norbornene derivative expressed with the example type of the 2nd composition (10) (Exo object)

The 5-norbornene endo-2 and 3-dicarboxylic anhydride 100g is made to react at 190 to 195 \*\* under a nitrogen atmosphere for 4 hours. 28g of 5-norbornene exo-2 and 3-dicarboxylic anhydrides were obtained by recrystallizing a reactant 5 times with toluene after radiational cooling (28% of yield). Next, the object was obtained by returning 5-norbornene exo-2 and 3-dicarboxylic anhydride in the same procedure as the synthetic example 1 (49% of yield). <sup>1</sup>H-NMR(CDCl<sub>3</sub>):delta(ppm)1.39-1.58 (2H, m), 2.47-2.71 (2H, m), 2.89 (1H, s) and 3.25 (1H, s), 3.95-4.03 (1H, m), 4.42-4.53 (1H, m), 6.1-6.35 (2H, m).

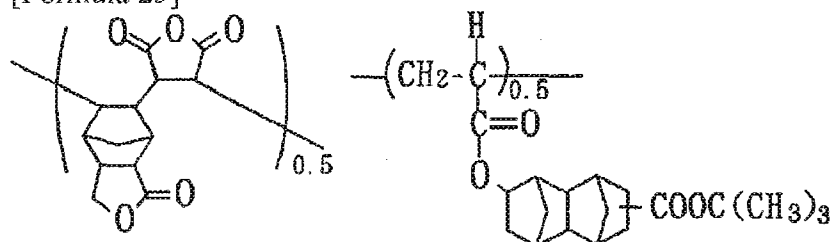
[0062]<> The norbornene derivative expressed with the example type of the 3rd composition (12) (an Endo object and R are methyl groups)

Like the synthetic example 1, it replaced with the 5-norbornene endo-2,3-dicarboxylic anhydride, and compounded using methyl-5-norbornene endo-2 and 3-dicarboxylic anhydride (the Wako Pure Chem make, product number 136-05955) (33% of yield).

[0063] <> Resin expressed with the 1st example type (23) (as for the norbornene derivative (1) and R<sup>1</sup> which have the lactone structure by which Z is shown in Table 1 in a general formula (5), a hydrogen atom and R<sup>2</sup> are t-butoxy KARUBONIRUTETORA cyclo dodecyl, x= 0.5, and y= 0.5)

[0064]

[Formula 23]



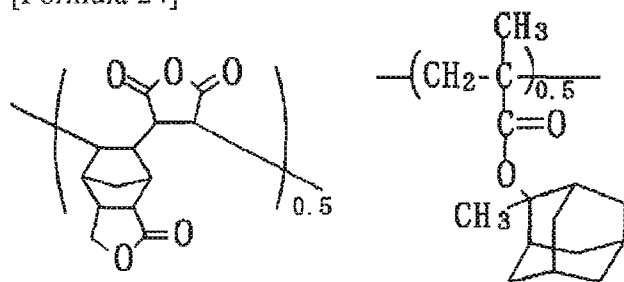
(23)

The norbornene derivative 2.26g, 1.475 g of maleic anhydrides, and 10 g of t-butoxycarbonyltetracyclododecylacrylate which were obtained in the synthetic example 2 are dissolved in THF30ml among the 100-ml eggplant flask which attached the refluxing pipe, 0.394 g of azobisisobutyronitrile (following azobisisobutyronitrile abbreviated \*\*) is added there, and heating flowing back is carried out under argon atmosphere. In 12 hours, it cools radiationally, and it flows into 500 ml of ether, and a \*\* exception carries out precipitate which deposited. 2.8g of objects were obtained by performing reprecipitation refining once again (20% of yield). The weight average molecular weight (Mw) calculated by GPC analysis was 6800 (polystyrene conversion), and the degree of dispersion (Mw/Mn) was 2.24.

[0065] <> Resin expressed with the 2nd example type (24) (as for a norbornene derivative (1) and R<sup>1</sup> which have the lactone structure by which Z is shown in Table 1 in a general formula (5), a methyl group and R<sup>2</sup> are a 2-methyl-2-adamantyl group, x= 0.5, and y= 0.5)

[0066]

[Formula 24]

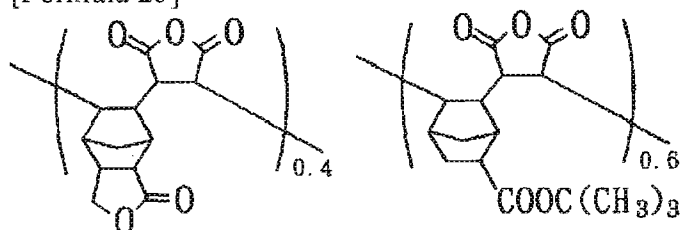


(24) Like Example 1, it replaced with t-butoxycarbonyltetracyclododecylacrylate and compounded using 2-methyl-2-adamantyl methacrylate (30% of yield). Mw=5400, Mw/Mn=2.34.

[0067] <> Resin expressed with the 3rd example type (25) (as for a hydrogen atom and R<sup>4</sup>, in the norbornene derivative (1) and R<sup>3</sup> which have the lactone structure by which Z is shown in Table 1 in a general formula (6), t-butyl group and c are 0, a= 0.4, and b= 0.6)

[0068]

[Formula 25]

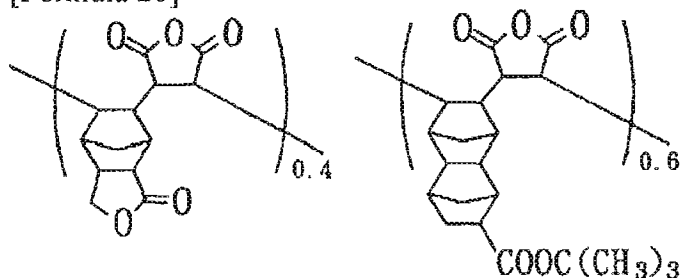


(25) The norbornene derivative 3g, 4.9 g of maleic anhydrides, and 5.82 g of 5-norbornene 2 \*\*KARUBON acid t-butylester which were obtained in the synthetic example 2 are dissolved in THF30ml among a 100-ml eggplant flask which attached a refluxing pipe, azobisisobutyronitrile 0.656g is added there and heating flowing back is carried out under argon atmosphere. In 12 hours, it cools radiationally, and it flows into 300 ml of ether, and a \*\* exception carries out precipitate which deposited. 5.76g of objects were obtained by performing reprecipitation refining once again (42% of yield). Mw=4800, Mw/Mn=2.28.

[0069]> Resin expressed with the 4th example type (26) (as for a hydrogen atom and R<sup>4</sup>, in a norbornene derivative (1) and R<sup>3</sup> which have the lactone structure by which Z is shown in Table 1 in a general formula (6), t-butyl group and c are 1, a= 0.4, and b= 0.6)

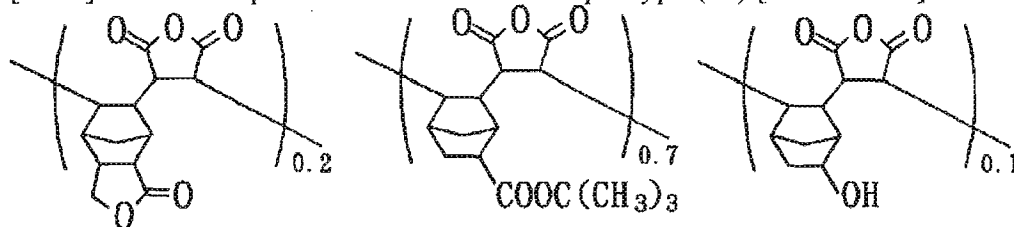
[0070]

[Formula 26]



(26) Like Example 3, it replaced with 5-norbornene 2 \*\*KARUBON acid t-butylester, and compounded using 3-tetracyclo dodecen 8-carboxylic acid t-butylester (31% of yield). Mw=8400, Mw/Mn=2.41.

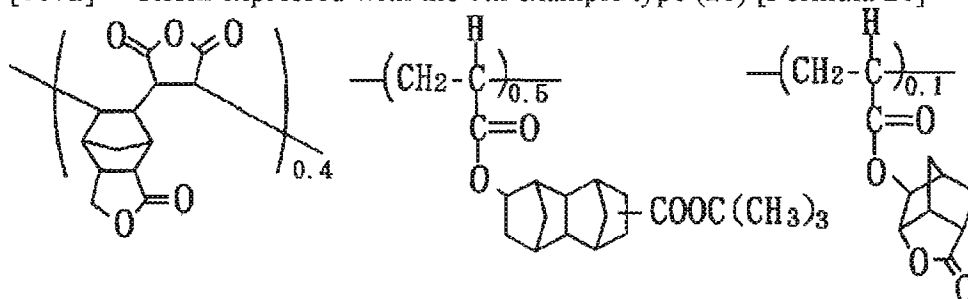
[0071]> Resin expressed with the 5th example type (27) [Formula 27]



(27) The norbornene derivative 2.3g, 5 g of maleic anhydrides, and 7.63 g of 5-norbornene 2 \*\*KARUBON acid t-butylester which were obtained in the synthetic example 1 among the 100-ml eggplant flask which attached the refluxing pipe, 0.56 g of 5-norbornene 2 \*\*ORU is dissolved in THF27ml, 0.67 g of azo-isobutyro-dinitrile is added there, and heating flowing back is carried out under argon atmosphere. In 12 hours, it cools radiationally, and it flows into 300 ml of ether, and a \*\* exception carries out

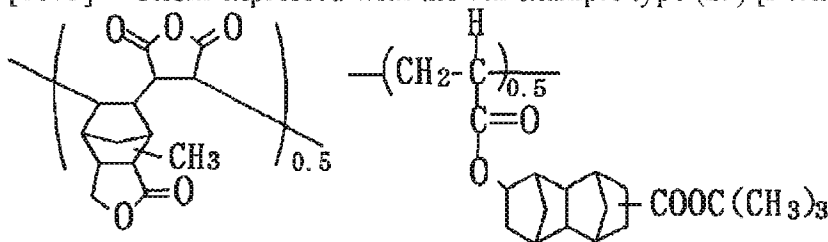
precipitate which deposited. 7.44g of objects were obtained by performing reprecipitation refining once again (48% of yield). Mw=7200, Mw/Mn=2.36.

[0072]<> Resin expressed with the 6th example type (28) [Formula 28]



(28) The norbornene derivative 2g, 1.3 g of maleic anhydrides, and 11.07 g of t-butoxycarbonyltetracyclododecylacrylate which were obtained in the synthetic example 2 among the 100-ml eggplant flask which attached the refluxing pipe, 1.37 g of 5-acryloyloxy 2,6-norbornane carbolactone is dissolved in THF28ml, 0.437 g of azo-isobutyro-dinitrile is added there, and heating flowing back is carried out under argon atmosphere. In 16 hours, it cools radiationally, and it flows into 300 ml of ether, and a \*\* exception carries out precipitate which deposited. 6.13g of objects were obtained by performing reprecipitation refining once again (39% of yield). Mw=10400, Mw/Mn=2.46.

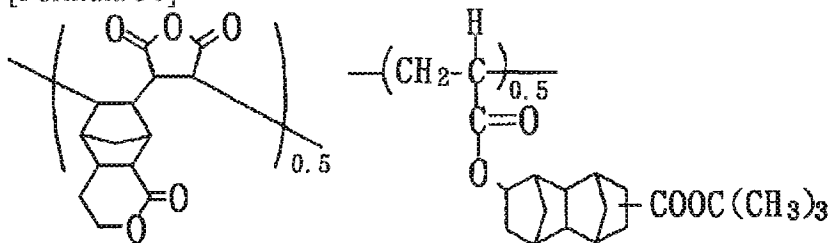
[0073]<> Resin expressed with the 7th example type (29) [Formula 29]



(29) It replaced with a norbornene derivative obtained in the synthetic example 2 like Example 1, and compounded using a norbornene derivative obtained in the synthetic example 3 (24% of yield). Mw=4600, Mw/Mn=2.41.

[0074]<> Resin expressed with the 8th example type (30) (as for a norbornene derivative (3) and R<sup>1</sup> which have the lactone structure by which Z is shown in Table 1 in a general formula (5), a hydrogen atom and R<sup>2</sup> are t-butoxy KARUBONIRUTETORA cyclo dodecyl, x= 0.5, and y= 0.5)

[Formula 30]

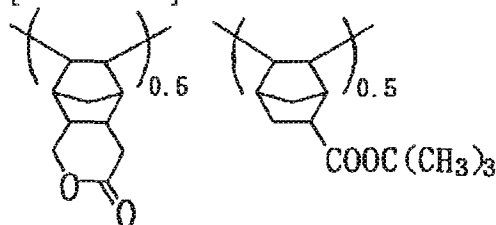


(30) A norbornene derivation object replaces [ that it might be the synthetic example 2 ]

with like Example 1, It compounded using 5,8-methano-3,4,4 a,5,8,8a-hexahydro 1H-2-benzopyran 1-one (J. it compounds by the method of Org.Chem., 50 volumes, No.25, T.Ikeda and others of a 5193 - 5199 pages (1985) statement) (18% of yield). Mw=4200, Mw/Mn=2.41.

[0075]<> Resin expressed with the 9th example type (31) (in 0 and R<sup>7</sup>, in a general formula (8), a hydrogen atom and R<sup>8</sup> are [ q / 1 and r / 1 and p ] t-butyl group and g=0.5.h=0.5)

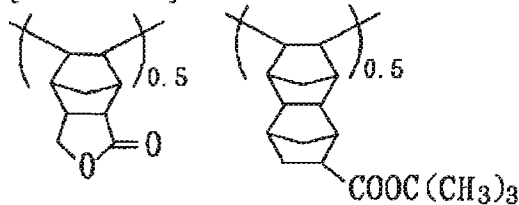
[Formula 31]



(31) Di-mu-chloroscrew [(eta-allyl) palladium (2)] 0.262 g and the hexafluoro silver antimonate 0.488g are dissolved in 44 ml of chlorobenzene, and it agitates at a room temperature. filtering a reaction mixture in 20 minutes -- a filtrate -- 5,8-methano-3,4,4 a,5,8,8a-hexahydro 3H-2-benzopyran 3-one (Tetrahedron Lett.) It adds to No.45 and the mixed liquor which serves as [ 4099 - 4102 pages (1976) ] 11.87 g of composition from 14.05 g of 5-norbornene 2-carboxylic acid t-butylester, 0.2 ml of water, and 170 ml of chlorobenzene by the method of H.Shimomura and others of a statement. After agitating it at a room temperature further for 20 hours, in addition to 1200 ml of methanol, a \*\* exception carries out depositing resin. Next, resin is dissolved in 150 ml of chlorobenzene, 30 ml of methanol and the sodium borohydride 3.2g are added there, and it agitates at a room temperature for 3 hours, and allows to stand at a room temperature further for 24 hours. A \*\* exception carries out the particles of Pd (0) which deposited, and 1000 ml of methanol is filled with a filtrate. 16.58g of target resin was obtained by a \*\* exception carrying out depositing resin (64% of yield). Mw=7100, Mw/Mn=2.34.

[0076]<> Resin expressed with the 10th example type (32) (in 1 and R<sup>7</sup>, in a general formula (8), a hydrogen atom and R<sup>8</sup> are [ q / 1 and r / 0 and p ] t-butyl group, g= 0.5, and h= 0.5)

[Formula 32]

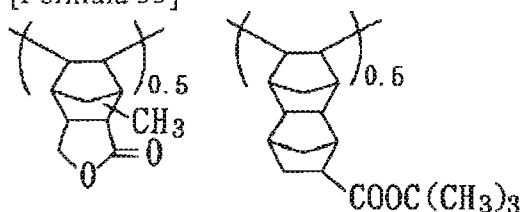


(32) It replaces with 5,8-methano-3,4,4 a,5,8,8a-hexahydro 3H-2-benzopyran 3-one like Example 9, It replaced with 5-norbornene 2-carboxylic acid t-butylester, using the monomer obtained in the synthetic example 2, and compounded using 3-tetracyclo dodecen 8-carboxylic acid t-butylester. 21% of yield, Mw=4300, Mw/Mn=2.44.

[0077]<> Resin expressed with the 11th example type (33) (in 1 and R<sup>10</sup>, in a general formula (9), a hydrogen atom and R<sup>11</sup> are [ R / a methyl group and w / 1 and w1 ] t-butyl group, g= 0.5, and h= 0.5)



[Formula 33]



(33) It replaces with 5,8-methano-3,4,4a,5,8,8a-hexahydro 3H-2-benzopyran 3-one like Example 9, It replaced with 5-norbornene 2-carboxylic acid t-butylester, using a monomer obtained in the synthetic example 3, and compounded using 3-tetracyclo dodecen 8-carboxylic acid t-butylester. 16% of yield, Mw=4100, Mw/Mn=2.52.

[0078](Evaluation of the etching resistance of resin) The resin 2g obtained in Example 1 was dissolved in 10 g of propylene-glycol-monomethyl-ether acetate, and, subsequently it filtered using a 0.2-micrometer Teflon (registered trademark) filter. Next, on a 3-inch silicon substrate, spin coat spreading was carried out, baking powder was performed on a hot plate for 90 \*\* and 60 seconds, and a thin film of 0.7 micrometer of thickness was formed. An etch rate [ as opposed to / using a Japanese \*\* Anelva make DEM451 reactive-ion-etching (RIE) device / CF<sub>4</sub> gas for an obtained film ] was measured (etching condition-ower=100W, a pressure = 5 Pa, gas mass flow =30sccm). The result is shown in Table 4. Similarly, an etch rate was measured also about resin obtained in Example 3 and Example 4, Example 9, Example 10, and Example 11. A result of a poly (methyl methacrylate) coating film which are poly (p-vinylphenol) currently used as a comparative example as base resin of novolac resist (Sumitomo Chemical Co., Ltd. make PFI-15A) and KrF resist and resin which does not have a bridged cyclic hydrocarbon group in molecular structure, either is also shown. An etch rate was standardized to novolac resist.

[0079]

[Table 4]

	エッチング速度(相対比)
実施例1で得た樹脂	1.1
実施例3で得た樹脂	1.15
実施例4で得た樹脂	1.0
実施例9で得た樹脂	1.1
実施例10で得た樹脂	0.9
実施例11で得た樹脂	0.85
ポリ(メチルメタクリレート)	1.9
ポリ(p-ビニルフェノール)	1.2
ノボラックレジスト(PFI-15A)	1

From the above-mentioned result, resin used by this invention had a slow etch rate to CF<sub>4</sub> gas, and excelling in dry etching resistance was shown.

[0080](Evaluation of the transparency of resin) The resin 2.5g obtained in Example 1 was dissolved in 10 g of propylene-glycol-monomethyl-ether acetate, and, subsequently it filtered using a 0.2-micrometer Teflon filter. Next, on a 3-inch quartz substrate, spin coat spreading was carried out, baking powder was performed on a hot plate for 90 \*\* and 60

seconds, and a thin film of 1 micrometer of thickness was formed. About this thin film, transmissivity at 193.4 nm which is a center wavelength of ArF excimer laser light was measured using spectrophotometer for ultraviolet and visible region (the Shimadzu make, UV-365). Similarly, it measured also about resin obtained in Example 3 and Example 4, and Example 10. As a result, in resin of 72%/0.5 micrometer, and Example 3, resin of 70%/0.5 micrometer, and Example 4 was [ resin which obtained transmissivity in Example 1 / resin of 69%/0.5 micrometer, and Example 10 ] 62%/0.5 micrometer. From this result, resin of this invention has checked that transparency available as monolayer resist was shown.

[0081](Patterning evaluation of resist) The resist which consists of the following presentation was prepared.

(a) resin (example 1): -- 2g (b) photo-oxide generating agent (triphenylsulfonium triflate (TPS)): -- 0.02g(c) propylene-glycol-monomethyl-ether acetate: -- use a 0.2-micrometer Teflon filter for the 11.5g above-mentioned mixture, [ pass and ] Resist was prepared. On a 4-inch silicon substrate, spin coat spreading of the above-mentioned resist was carried out, bake was carried out on the hot plate for 130 \*\* 1 minute, and the thin film of 0.39 micrometer of thickness was formed. And the wafer which formed membranes in the stuck type exposure experimental aircraft enough purged with nitrogen was settled. The mask which drew the pattern with chromium on the quartz plate was stuck on the resist film, and it irradiated with ArF excimer laser light through the mask. Bake was immediately carried out on the hot plate for 120 \*\* and 60 seconds after that, the 2.38%TMAH solution of 23 \*\* of solution temperature performed development by dip coating for 60 seconds, and pure water performed rinsing treatment for 60 seconds continuously, respectively. As a result, dissolution removal only of the exposed part of a resist film was carried out at the developing solution, and the pattern of the positive type was obtained. The resist using the resin obtained in the resin similarly obtained in Example 3 and Example 4, and Example 10 was also evaluated. The result of sensitivity and resolution is shown in Table 5.

[0082]

[Table 5]

	解像度 ( $\mu\text{mL/S}$ )	感度 ( $\text{mJ}/\text{cm}^2$ )
実施例1の樹脂を含有するレジスト	0.19	9
実施例3の樹脂を含有するレジスト	0.20	6.5
実施例4の樹脂を含有するレジスト	0.20	8
実施例10の樹脂を含有するレジスト	0.20	7

The above result showed that the positive type chemical amplification resist of this invention had outstanding resolution characteristics. Since there were no phenomena, such as pattern peeling, it has checked excelling also in substrate adhesion.

[0083]As mentioned above, although the example of this invention has been explained in full detail, concrete composition is not restricted to this example, and even if there are change etc. of a design of the range which does not deviate from the gist of this invention, it is included in this invention. .

[0084]

[Effect of the Invention]Since the resin which has alicyclic lactone structure was used for

the main chain according to resin for resist of this invention, chemical amplification type resist, and the pattern formation method using it as explained above, The positive type chemical amplification resist which was excellent in dry etching resistance and transparency, and also was excellent in resolution and substrate adhesion is obtained, and minute pattern formation required for semiconductor device manufacture is possible.

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[Translation done.]